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TOXIC METAL SPECIATION SCHEME FOR WATER AND SEDIMENT FROM AN URBAN STORM SEWAGE

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Abstract : Taking into account available metal speciation schemes for river water and sediments, we have developed a scheme designated to evaluate the metal toxicity of urban storm water and sediment samples and containing 3 dissolved and 5 particulate fractions. Reagents and procedures for determination of total particulate metals have been compared, together with ion exchangeable and carbonate fractions. This speciation scheme was applied to urban storm sewage samples : it was observed that dissolved lead, zinc and cadmium were mainly concentrated in the labile fraction and that each particulates metal was distributed differently.

Keywords : cadmium, carbonate, dissolved metal, hydroxides, iron, lead, manganese, oxides, particulate metal, sediments, speciation, urban storm sewage, water, zinc.

1. Introduction

Since several years it has been shown in several countries that water bodies quality does not follow efforts spent on development of sewer networks and treatment plants. Among various diagnostics of present failures, urban storm drainage has to be considered (*Torno, Marsalek and Desbordes, 1986*) since it contains large amounts of toxic metals such as lead, zinc and cadmium, which may, either dissolved or fixed on suspended matter or sediments, reach rivers, lakes or estuaries (*Bachoc and Thévenot, 1987*). Its impact upon receiving waters is thus greatly dependent upon the mobility of these dissolved or particulate metals and their accessibility to living cells.

This paper presents how, taking into account available metal speciation schemes for river water and sediments, we have developed and tested a scheme for dissolved and particulate toxic metal contained in urban storm sewage (*Flores-Rodriguez and Thévenot, 1988*).

2. Material and Methods

Water and sediments were sampled in the "La Morée" rain sewage which drains urban runoff water from a residential area of an east suburb of Paris in Seine-Saint-Denis Department and further reaches Seine river.

After transport and storage at 4°C, samples were separated into dissolved and particulate fractions using a 30 min 6,500 rpm centrifugation (Jouan, model Plasma CR 1000) followed by tangential membrane filtration (Millipore, model Minitan S) using 0.45 μm Millipore Durapore membranes. These membranes were previously soaked into 10 % HNO_3 during 72 hr, rinsed with bidistilled ultrapure water (Millipore, milli-Q), soaked into 2 M $Ca(NO_3)_2$ during 2 hr and finally rinsed with bidistilled ultrapure water.

Dissolved lead, zinc and cadmium were determined either directly by atomic absorption spectrophotometry (AAS) (Perkin Elmer, model HGA 700 with AS 70 sampler), giving the total dissolved metal amount, or after speciation. Three fractions were determined :

a. free, or very labile metal, as measured by anodic stripping differential pulse polarography (ASDPP) in pH 6.5 acetate buffer (PAR-EGG model 364 with 303 static mercury drop electrode),

b. free and labile metal, as measured by the amount fixed by 24 hr equilibration of 50 ml sample with 0.5 g Chelex 100 resin, previously soaked into 1 M $CaCl_2$ solution and rinsed with ultrapure water,

c. stable metal, measured in the supernatant of the batch treatment with Chelex 100 resin, i.e. complexes more stable than resin affinities for these metals.

Particulate lead, zinc, cadmium, iron and manganese were determined either directly after 2 hr calcination at 550°C and mineralisation by a 30 % HCl, 40 % HF 1/1 mixture at 110°C (twice) and by a 65 % HNO_3, ultrapure water 3/10 mixture at 110°C, or after successive chemical treatments. In all cases, samples were 15 min centrifuged at 6,500 rpm, rinsed twice with 5 ml ultrapure water and supernatants analysed by flame or furnace atomic absorption spectrophotometry. Five successive particulate fractions were determined from 2 g (fresh weight) sediments :

a. ion exchangeable fraction was released after 2 hr stirring at room temperature with 20 ml 1 M $CH_3CO_2NH_4$ solution at pH 7.0,

b. carbonate fraction was released after 2 hr stirring at room temperature with 20 ml 1 M CH_3CO_2H - CH_3CO_2Na buffer at pH 5.0,

c. iron and manganese oxides and hydroxides fraction was released after 5 hr stirring at 85°C with 20 ml 0.04 M NH_2OH, HCl solution in 25 % CH_3CO_2H,

d. organic matter fraction was released after 3 hr digestion at 96°C with 20 ml 30 % H_20_2 into 0.02 M HNO_3, followed by 2 hr digestion at 96°C with 6ml 30 % H_20_2 and 1 hr stirring at room temperature with 10 ml 1M $CH_3CO_2NH_4$ into 6 % HNO_3,

e. residual fraction was released by complete digestion into a 12 ml 70 % $HClO_4$-40 % HF 2/10 mixture at 110°C followed by complete digestion into 2 ml 70 % $HClO_4$ at 110°C and, finally, digestion into 13 ml 65 % HNO_3 ultrapure water 3/10 mixture during a few min at 110°C.

All chemicals used to prepare reagents and standards were of highest available purity and vessels were washed in 2% Extran (Merck MA02), 10% HNO_3 and rinsed 4 times with distillated water and once with milli-Q water.

3. Speciation scheme determination and evaluation

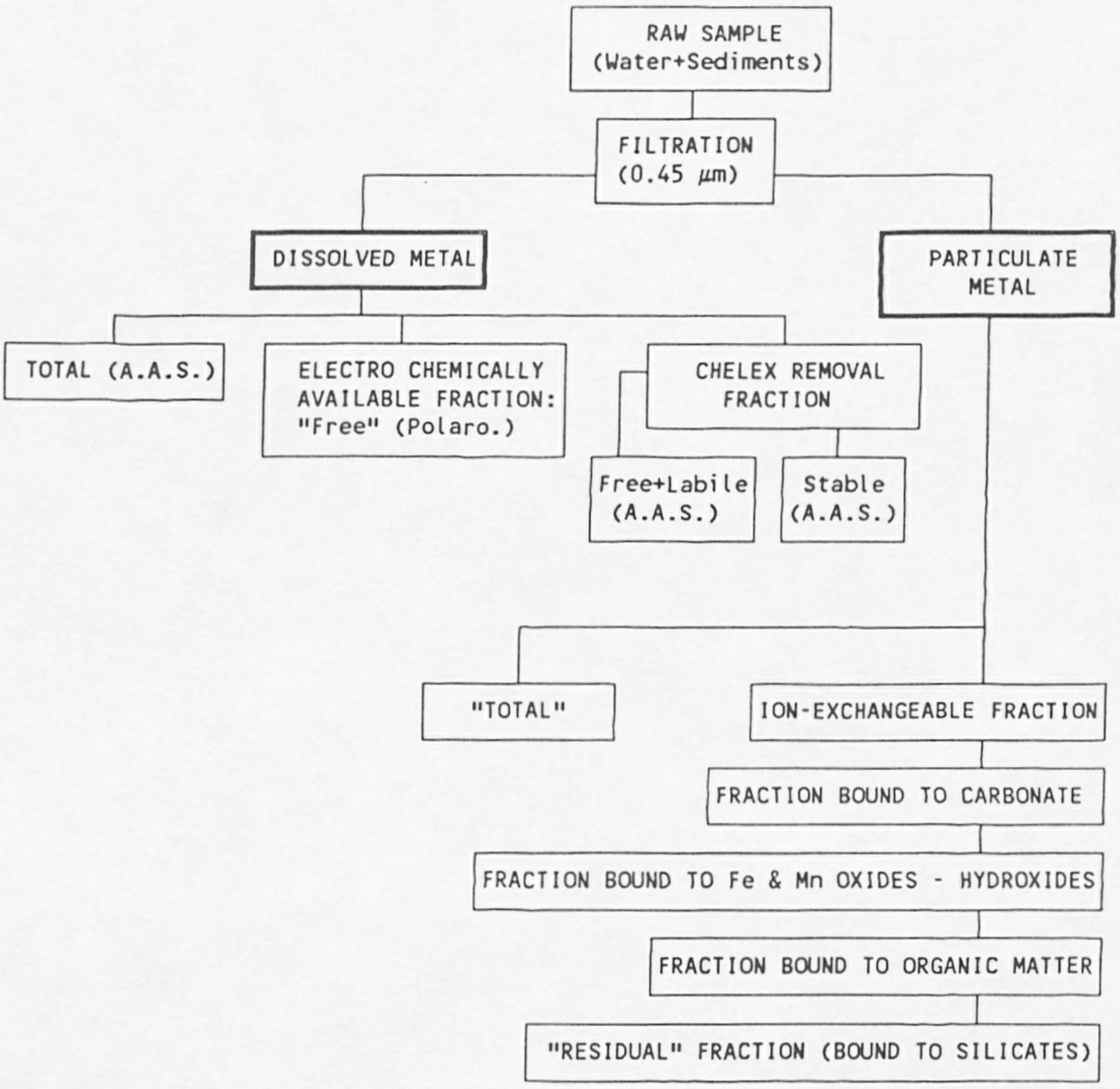

Figure 1 Dissolved and particulate metal speciation scheme for urban storm sewage.

3.1. Dissolved metal

The standard method for dissolved fraction separation is generally filtration through membranes which *porosity* equal 0.45 μm. We have found convenient and more rapid to precede such filtration by centrifugation and to then to use either nitrogen gas pressurized ultrafiltration cells or tangential filtration modules.

Several dissolved metal speciation schemes have been developed for river or reservoir water samples. *Florence and Batley (1977)* suggest to separate 7 fractions using UV and Chelex 100 treatments and anodic stripping polarography. *Figura and Mc Duffle (1979)* simplify the latter scheme using only batch and column Chelex treatment, acid digestion and anodic stripping polarography (4 fractions). The same authors *(1980)* further added a 5^{th} fraction, using acid digestion of both the total dissolved fraction and Chelex 100 supernatant in batch experiments. *Lecomte et al. (1981)* introduced anion and cation exchange resins in columns, in order to discriminate cationic and anionic metal species, and compared atomic absorption spectroscopy and anodic stripping polarography analysis for discriminating free and total metal amounts of each fraction (8 fractions).

In order to simplify dissolved metal speciation scheme and to limit its duration, we preferred to follow *Morrison and Revitt (1987)* scheme which contains only 3 fractions (free, labile and stable) determined by 3 measurements, i.e. total, electrochemically active and not fixed by batch equilibrium with Chelex 100 metal complexing resin. This scheme, summarized on Figure 1, was found reliable and informative for all urban runoff water samples *(Flores-Rodriguez et al. 1990)*

3.2 Particulate metal

3.2.1 Total particulate metal

Assessment of total particulate metal is performed after mineralisation of samples by successive reactions of strong acids in teflon beakers. A typical procedure used for river sediments contains 5 steps: 12 ml 40 % HF - 70 % $HClO_4$ 10/2 mixture at 110°C, followed by 2 ml 70 % $HClO_4$ at 110°C, by 13 ml 65% HNO_3 - milli-Q water 3/10 mixture at 110°C and 15 ml milli-Q water rinsing, 15 min 6,500 rpm centrifugation, supernatant separation, another 5 ml milli-Q water rinsing, 15 min 6,500 rpm centrifugation and supernatant separation.

In the urban storm sewage sediments sampled for this study, we faced spontaneous ignition or explosion during some of these acid treatments. Thus we compared several procedures using different reagent composition and sequence :

a. 12 ml 65 % HNO_3 - 70 % $HClO_4$ 10/2 mixture at 110°C, rinsing and centrifugation (twice),
b. 20 ml 30 % H_2O_2 - 0.02 N HNO_3 1/1 mixture at 85°C during 2 hr and 6 ml 30 % H_2O_2 at 85°C during 3 hr, rinsing and centrifugation (twice),
c. 10 ml 30 % HCl - 65 % HNO_3 1/4 mixture at 110°C, followed by 10 ml 40 % HF at 110°C and 13 ml 65 % HNO_3 - milli-Q water 3/10 mixture, rinsing and centrifugation (twice),
d. 2 hr calcination at 550°C followed by HCl - HF and HNO_3 mineralisation (see Material and Methods).

Comparison of 5 metal amounts in the same sewage sample treated by these 4 methods (Table 1) shows differences for each metal, no procedure giving the highest metal amount for all metals. Although a calcination prior to mineralisation yielded significant loss of iron, zinc and cadmium, we found that this last method was superior to others since, on the contrary to others, it never gave us any spontaneous ignition or explosion with sewage, retention pound or road sediment samples.

Procedure	Zn	Pb	Cd	Fe	Mn
$HNO_3/HClO_4$	1100	571	17,2	20140	276
$H_2O_2/HNO_3 + H_2O_2$	1257	498	17,9	19345	245
$HCl/HNO_3 + HF + HNO_3$	1455	548	11,2	16333	203
Calcination + $HCl/HF + HNO_3$	775	962	6,8	16400	250

Table 1. Comparisons of different reagents for total particulate metal determination. (See text for experimental details)

3.2.2. Particulate metal speciation schemes

Since toxic metals have been found to be concentrated on particulates either by adsorption, ion-exchange, chelation or coprecipitation reactions (*Meguellati, 1982*), we found important to evaluate their

biodisponibility by successive extractions with chemical reagents. *Engler et al. (1974)* suggested to separate 6 fractions : interstitial water, ion exchangeable, easily reducible, organic, moderately reducible and residual. *Tessier et al. (1979)* introduced a carbonate and iron/manganese oxides and hydroxides fractions and did not take into account interstitial water nor the moderately reducible fraction. *Salomons and Förstner (1980)*, using 7 fractions incorporated previous protocols and introduced a non-silicate iron fraction. *Gambrell et al. (1980)* spent effort to distinguish 2 organic fractions (total 6 fractions). In order to simplify these speciation schemes, *Meguellati (1982)* distinguished 5 fractions (ion-exchangeable, organic, carbonates, reducible and silicate) whereas *Welté and Montiel (1983)* reintroduced the moderately reducible fraction and placed the organic and sulphide extraction by H_2O_2 after the carbonate and oxides hydroxides extractions. The most recent speciation scheme suggested by *Morrison and Revitt (1987)* presents only 3 fractions, incorporating in a single extract carbonates and oxides/hydroxides fractions and not measuring the residual metals. Within these different speciation schemes, we have tried to compromise between simplicity and quality of available informations by chosing an intermediate between *Meguellati (1982)* and *Welté and Montiel (1983)* schemes : thus we have selected 5 successive extracting reagents which are supposed to discriminate ion exchangeable, carbonates, oxides/hydroxides, organic matter and residual fractions (Figure 1).

A large discussion has developed for the first 2 extraction reactions, i.e. ion exchangeable and carbonates, and their mutual independence. In order to evaluate 3 different reagents for ion-exchangeable fraction and 2 reagents for carbonate one, we have conducted 5 speciation schemes on the same sewer sediment sample :

1. 20 ml 1 M $CH_3CO_2NH_4$ at pH 7 followed, after centrifugation and separation of supernatant, by 15 ml 1 M CH_3CO_2H, and 3 following extractions described in Material and Methods,
2. 20 ml 1 M $CH_3CO_2NH_4$ at pH 7 followed by 20 ml 1 M CH_3CO_2H/CH_3CO_2Na buffer at pH 5,
3. 20 ml 1 M $Mg(NO_3)_2$ at pH 7 followed by 20 ml 1 M acetate buffer at pH 5,
4. 20 ml 1 M $BaCl_2$ at pH 7 followed by 15 ml 1 M acetic acid,
5. 20 ml 1 M $BaCl_2$ at pH 7 followed by 20 ml 1 M acetate buffer at pH 5.

Results presented in Table 2 shows that first extraction with ammonium acetate (methods 1 and 2) gives higher iron levels, but also higher zinc, cadmium and manganese ones (results not shown). Results for lead are not significant for this fraction. pH 5 acetate buffer (protocols 2, 3 and 5) gives, for the second extraction, the highest lead, iron, zinc and cadmium levels suggesting that this reagent is more active than 1 M acetic acid. Thus we finally decided, in accordance with *Salomons and Förster (1980)* results, to use ammonium acetate as first extracting reagent and pH 5 acetate buffer as second one (method 2) : this milder reagent is indeed less aggressive towards iron and manganese oxides/hydroxides (*Welté and Montiel, 1983*) and organic matter (*Jouanneau et al. 1983*) especially humic acids (Meguellati 1982).

	Lead (mg/kg dry weight)					Iron (mg/kg dry weight)				
	Procedures					Procedures				
	1	2	3	4	5	1	2	3	4	5
Fractions:										
ion-exchangeable	0.0	0.0	0.7	1.2	0.0	45	50	41	32	27
carbonates	3.9	11.5	19.7	0.0	11.5	2334	5849	6597	2676	4504
oxides/hydroxides	43.9	80.2	79.8	95.9	66.2	3900	2880	2082	4880	2520
organic matter	417.7	407.7	528.2	67.8	74.8	2027	1787	1485	2939	1626
residual	168.0	37.8	86.7	252.0	301.2	8865	5615	8172	6750	9500
Sum	633.5	537.2	715.1	416.9	453.7	17171	16181	18377	17277	18177

Table 2. Comparison of procedures for ion-exchangeable and carbonate fractions of particulate Lead and Iron speciation: Ammonium acetate pH 7 + acetic acid (1), ammonium acetate pH 7 + acetate buffer pH 5 (2), magnesium nitrate + acetate buffer pH 7 (3), barium chloride pH 7 + acetic acid (4) and barium chloride pH 7 + acetate buffer pH 5 (5) (See text for experimental details).

Finally, a duplication of this reaction scheme on the same sediment sample has shown that the speciation dispersion of zinc, lead, cadmium, iron and manganese is lower than 10 % for all fractions and that analytical dispersion is lower than 4 %.

3.3 Results

Figure 2 shows that, in the small amount of dissolved lead present in "La Morée" sewage sample, more than the half is labile, i.e. weakly complexed and thus relatively easily bioavailable; similar results have been obtained for cadmium (100 % labile) and zinc (74 % labile) and other sewage, detention ponds and road sewage samples.

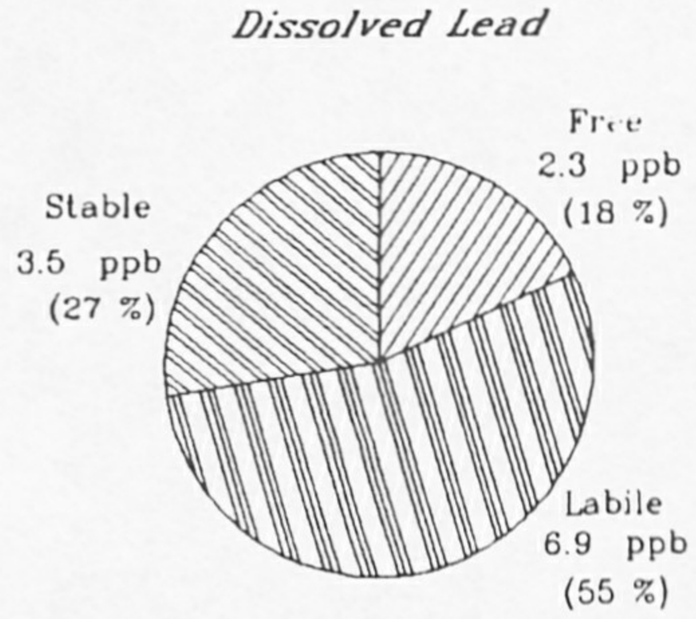

Figure 2 Speciation of dissolved lead in "La Morée" urban storm sewage: amounts in each fractions are expressed in µg/l or ppb and in percentage (See text for experimental conditions).

Figure 3 presents the distribution of lead and iron in sediments present in the same sample. It shows that this distribution depends greatly upon the analysed metal : although lead is almost entirely present in the organic matter fraction, iron is mainly shared between carbonate and residual ones. Cadmium is almost entirely present in oxides/hydroxides fraction (86 %) and zinc shared between oxides/hydroxides and organic matter (52 and 35 % respectively). Although differences have been observed in other sediments sampled in urban storm sewage, detention ponds or road sewage, a common behaviour seems to be, in accordance with Giroud (1984) results, the quasi-absence of metals in the ion-exchangeable fraction (Flores-Rodriguez et al. 1990). It is clear that the origin of these samples and the source of metal release play an important role on this distribution.

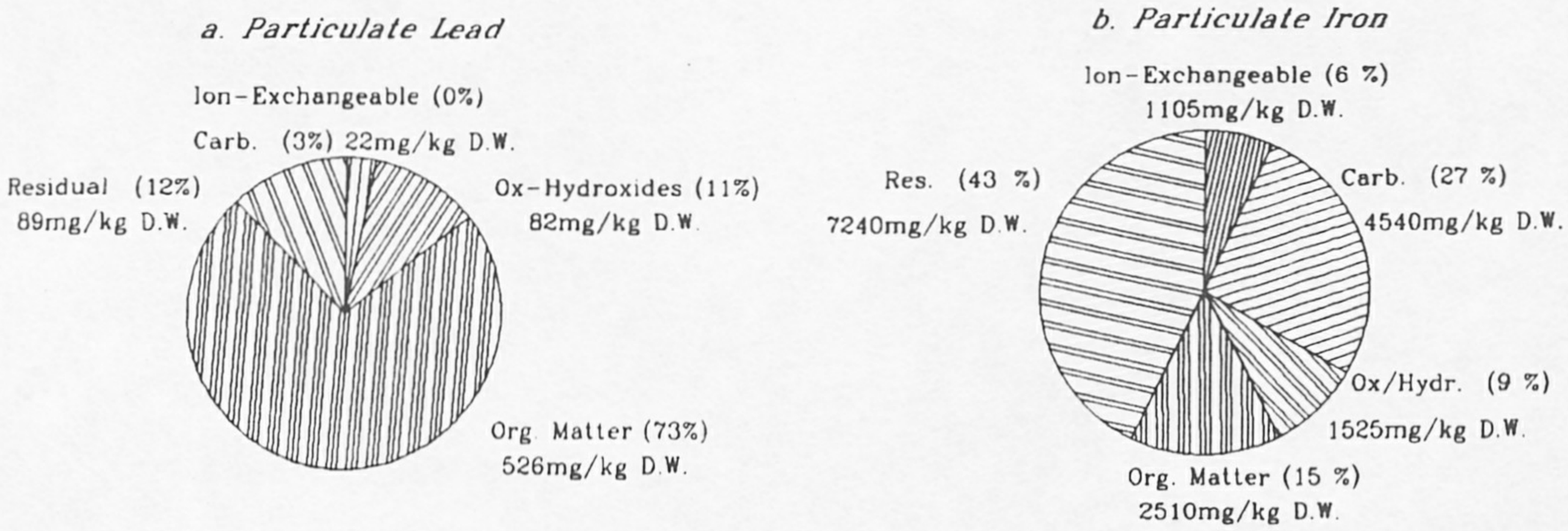

Figure 3 Speciation of particulate Lead (a) and Iron (b) in "La Morée" urban storm sewage: amounts in each fraction are expressed in mg/kg dry weight or ppm and percentage (See text for experimental conditions).

4. Conclusion

This paper presents a dissolved and particulate metal speciation scheme derived from the one suggested by *Morisson and Revitt (1987).* Although we are convinced that none of the numerous available speciation scheme, including this one, is exempt of failure or drawbacks, particularly for the specificity of the successive extractions performed on sediments, we feel that they may bring useful informations

about the bioavailability and geochemical mobility of toxic metal in urban storm runoff water and sediments.

These informations are of high importance for the assessment of urban runoff upon receiving waters and for the design of treatment procedures. This scheme has been applied to water and sediment sampled in other separative sewage networks as well as in wet detention ponds and road sewage (Flores Rodriguez et al. 1990). Ungoing research is devoted to dry detention ponds fed by separative or waste water during storms.

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